A phase-separation perspective on dynamic heterogeneities in glass-forming liquids

C. Cammarota,[1,*] A. Cavagna,[2] I. Giardina,[2] G. Gradenigo,[3] T. S. Grigera,[4] G. Parisi,[5] and P. Verrocchio[6]

[1] *IPhT, CEA Saclay, France*

[2] *Centre for Statistical Mechanics and Complexity (SMC), CNR-INFM.*

[3] *CNR-ISC and Dipartimento di Fisica, Università Sapienza*

[4] *INIFTA and Departamento de Física, Universidad Nacional de La Plata, and CCT La Plata*

[5] *Dipartimento di Fisica, Sapienza Università di Roma*

[6] *Dipartimento di Fisica, Università di Trento*

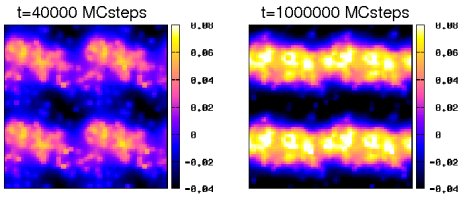

FIG. 1. Fluctuations of the overlap field for the constrained dynamics with $\hat{Q} = 0.25$. $\tau_\alpha = 40000$ MC steps.

The conspicuous lack of a growing correlation length, contrasting with the very steep increase of the relaxation time, has been a puzzle in the physics of structural glasses for quite a long time. The first breakthrough has been the discovery of dynamic heterogeneities and the detection of a growing dynamical correlation length ξ_d [1]. Dynamic heterogeneities show up as regions with very different mobility of the particles during a time lag comparable to the α relaxation time, τ_α. Pure thermodynamics is involved in the definition of a completely different correlation length, ξ_s, discovered more recently: the Point to Set length [2]. This length is naturally determined in the Random First Order Theory by the balance between the amorphous surface tension cost and the configurational entropy gain of any rearrangement [3]. An important issue is the unification of the dynamic and the thermodynamic frameworks, so as the understanding of the interplay between the two correlation lengths.

Although the static-dynamic connection is clear in mean field systems and in some more realistic systems [4], we are quite far from a unifying picture in real glass-formers. We face this problem studying dynamic heterogeneities in a glass-forming liquid with constrained global overlap. This approach shows that the surface tension, which is a crucial ingredient of the thermodynamic framework, also plays a key role in the formation of dynamic heterogeneities.

Dynamic heterogeneities usually show a time-dependent size $\xi(t)$ with a maximum $\xi(\tau_\alpha) = \xi_d$. Beyond τ_α the system loses the memory of its initial configuration, i.e. the mobility becomes large everywhere, and there is no signal showing spatial heterogeneity in the dynamics. The large time behaviour of a dynamics in which the system cannot entirely lose memory of its initial configuration would be completely different. We have implemented this dynamics by imposing a lower bound $\hat{Q}$ on the overlap $Q(t)$. This quantity measures the similarity between an equilibrium initial configuration taken as a reference configuration, and the configuration at t. In the unconstrained dynamics $Q(t \gg \tau_\alpha)$ is 0. The constrained dynamics shows the same behaviour of the uncostrained one at short time t, including the growth of the dynamic heterogeneities. Yet, at large t things necessarily change as we reject all the particle movements which do not fulfill the constraint $Q(t) \geq \hat{Q}$. Two alternative hypoteses are possible for the large time behaviour of the constrained system. Heterogeneities, just grown during the unperturbed short time regime, may shrink back towards a large time configuration in which particles with low and high mobility are spread across all the system. A second possibility is that heterogeneities merge letting $\xi(t)$ grow beyond ξ_d and driving the system towards a phase separated highly correlated state. The first scenario would be incompatible with the existence of a surface tension cost of any rearrangements. On the contrary, the second picture is the expected one in presence of a non-zero surface tension. In this case a merging of the rearranged regions would be preferable since the system pays a smaller global interface cost.

Inspection of the constrained dynamics at large t gives evidence for phase separation of the system into high and low mobility regions, the picture naturally expected in presence of a non-zero surface tension. The enlarging of the dynamic heterogeneities is less marked when the temperature is higher. This is consistent with the idea that the surface tension decays at high temperature [5]. Moreover we find that the decrease of the global energy is compatible with the coarsening process in systems undergoing phase separation [6]. Finally fluctuations of the order parameter around the value $\hat{Q}$ reveal the outline of an effective thermodynamic potential [7] which shows evidence of the Maxwell construction, i.e. the landmark of phase separation.

* Corresponding author: chiara.cammarota@cea.fr

[1] Annu. Rev. Phys. Chem. **51**, 99 (2000); Phys. Rev. Lett. **82**, 5064 (1999); J. Non-Cryst. Sol. **307**, 215 (2002).
[2] J. Chem. Phys. **121**, 7347 (2004); Nat. Phys. **4**, 771 (2008).
[3] Phys. Rev. A **40**, 1045 (1989).
[4] Math. Theor. **40**, F251 (2007).
[5] J. Stat. Mech. L12002 (2009); J. Chem. Phys. **131**, 194901 (2009).
[6] Adv. Phys. **43**, 357 (1994).
[7] Physica A **261**, 317 (1998).